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IR luminescence from the $^{1}G_{4}$ multiplet of Pr$^{3+}$ in various doped crystals

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Abstract

Emission spectra, Stark component positions and fluorescence dynamics of the directly excited $^{1}G_{4}$ multiplet of Pr$^{3+}$ in various oxide or fluoride crystals have been studied.

Introduction

The interest in the Stark component positions and lifetime of the $^{1}G_{4}$ multiplet of Pr$^{3+}$ in doped materials is mainly due to the fact that the $^{1}G_{4} \rightarrow ^{3}H_{5}$ fluorescence takes place at about 1.3μm in the transmission window of fibers and is usable for optical amplification and laser emission. Another interest is that pumping close to this level in the near IR may lead to blue ($^{3}P_{0} \rightarrow ^{3}H_{4}$) or orange ($^{1}D_{2} \rightarrow ^{3}H_{4}$ or $^{3}P_{0} \rightarrow ^{3}H_{6}$) emissions by up-conversion to one of the $^{3}P_{J}$ or $^{1}I_{6}$ manifolds [1]. However, few spectroscopic properties of the $^{1}G_{4}$ multiplet have been reported for crystals, less than in the case of glasses or fibers.

This paper compares the properties of the $^{1}G_{4}$ multiplet in several Pr$^{3+}$ doped crystals: oxides, Y$_{3}$Al$_{5}$O$_{12}$ and YAlO$_{3}$, or fluorides, LiYF$_{4}$, BaY$_{2}$F$_{8}$ and LaF$_{3}$.

Excitation and emission spectra

They have been recorded at 4.4K with a c.w. Tisapphire laser (resolution 2 GHz) pumped with an Ar laser (figures 1 and 2). Such spectra have never been published to our knowledge, contrary to the $^{3}P_{0}$ or $^{1}D_{2}$ ones. These experiments are in progress for LaF$_{3}$.

The table 1 gives the position of the Stark components of the $^{1}G_{4}$ multiplet, which have been observed according to symmetry and selection rules. They have been verified with the help of the absorption spectra and the $^{3}P_{0}$ or $^{1}D_{2}$ emission spectra. They confirm and precise the literature data for Y$_{3}$Al$_{5}$O$_{12}$ [2] and LiYF$_{4}$ [3]. For YAlO$_{3}$ and BaY$_{2}$F$_{8}$, the whole energy level scheme, completing previous reports [4], will be published elsewhere.
Figure 1: $^1G_4 \rightarrow ^3H_5$ unpolarized emission spectra at 4.4K

Figure 2: $^3H_4 \rightarrow ^1G_4$ excitation spectra at 4.4K
The table 2 gives the wavelengths of the most intense lines of the emission from $^1\text{G}_4$ to the lowest Stark components of $^3\text{H}_5$. They are in agreement with the literature data on the $^3\text{H}_5$ Stark components. We have also recorded the weaker $^1\text{G}_4\rightarrow^3\text{H}_4$ spectra, which confirm the $^3\text{H}_4$ Stark splittings.

Table 2: Fluorescence line wavelengths (mm) related to the emission from $^1\text{G}_4$ to the lowest Stark components of the $^3\text{H}_5$ level.

<table>
<thead>
<tr>
<th>YAG</th>
<th>YAP</th>
<th>YLF</th>
<th>YBF</th>
</tr>
</thead>
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<tr>
<td>9712</td>
<td>9590</td>
<td>9699</td>
<td>9712</td>
</tr>
<tr>
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</tr>
<tr>
<td>10284</td>
<td>10219</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1: $^1\text{G}_4$ observed energy levels (cm$^{-1}$).

$^1\text{G}_4$ fluorescence decays

They have been recorded with a cooled Ge detector (response time 0.4μs) on a Lecroy digital oscilloscope, when monitoring the most intense $^1\text{G}_4\rightarrow^3\text{H}_5$ emission after exciting into one of the $^1\text{G}_4$ Stark components with a YAG pumped, Raman-shifted, pulsed dye laser.

The room temperature and 12K decays are exponential over almost 3 decades, except for LiYF4. The experimental decay times (table 3) are compared to the radiative decay times, given in literature [14,15] or calculated in this work using published Judd-Offelt parameters [11-13].

It appears that the $^1\text{G}_4$ decays, in such low Pr$^{3+}$ concentrated crystals, are dominated by multiphonon nonradiative relaxations, as the experimental decay times are clearly shorter than the calculated radiative lifetimes, the contributions of which are negligible, except for LaF3. Going down the table, from oxides to fluorides, the decay rate decreases in agreement with the increase of the number of phonons p involved in the nonradiative de-excitation and estimated as the ratio between the energy gap $\Delta E$ from the lower $^1\text{G}_4$ level to the higher $^3\text{F}_4$ level and the maximum phonon energy $h\omega$. The experimental nonradiative decay rate $W_{NR}$, calculated with the formula $\tau_{rad}^{-1} = \tau_{rad}^{-1} + W_{NR}$, are compared to the values calculated with the empirical "gap law": $W_{NR}(0)=\beta \exp(-\alpha\Delta E)$ [17]. The evolution is coherent but the agreement between the numerical values is not always good, emphasizing, as often, the approximative character of the "gap law". It can be noticed that the ratio of the decay rates at R.T. and 12K is satisfactorily accounted for by the empirical formula $W_{NR}(T)=W_{NR}(0) [\exp(h\omega /kT)/\exp(h\omega /kT)-1]$. 

\[
\tau_{rad}^{-1} = \tau_{rad}^{-1} + W_{NR}
\]

\[
W_{NR}(0)=\beta \exp(-\alpha\Delta E)
\]

\[
W_{NR}(T)=W_{NR}(0) [\exp(h\omega /kT)/\exp(h\omega /kT)-1]
\]
The behavior of LiYF4 appears different from that of other crystals: the decays are not exponential, especially at low temperature. This can probably be explained by energy transfer and cross-relaxation, due to higher Pr$^{3+}$ concentration. At room temperature the decay is less non-exponential than at 12K probably because of energy diffusion.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>[Pr$^{3+}$] (%)</th>
<th>$\tau_{\text{exp}}$(R.T.) ($\mu$s)</th>
<th>$\tau_{\text{exp}}$(12K) ($\mu$s)</th>
<th>$^{1}G_4-^{3}F_4$ gap (cm$^{-1}$)</th>
<th>Phonon energy (cm$^{-1}$)</th>
<th>$\tau_{\text{rad}}$ (ms)</th>
<th>$W_{\text{exp}}^{\text{NR}}$ (s$^{-1}$)</th>
<th>$W_{\text{exp}}^{\text{NR}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG</td>
<td>0.08</td>
<td>0.5</td>
<td>0.5</td>
<td>2222 [2]</td>
<td>865 [6]</td>
<td>0.92 [11]</td>
<td>2.10$^6$</td>
<td>2.2$^6$ [16]</td>
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<tr>
<td>YAP</td>
<td>0.1</td>
<td>0.86</td>
<td>0.86</td>
<td>2202</td>
<td>780 [7]</td>
<td>1.31 [12]</td>
<td>1.2.10$^6$</td>
<td>2.10$^5$ [17]</td>
</tr>
<tr>
<td>YBF</td>
<td>0.1</td>
<td>38</td>
<td>89</td>
<td>2465</td>
<td>415 [9]</td>
<td>2.29 [14]</td>
<td>1.0810$^4$</td>
<td>2.10$^3$ [17]</td>
</tr>
</tbody>
</table>

Table 3: $^{1}G_4$ fluorescence decay parameters.

Conclusion

Emission spectra and fluorescence dynamics of the directly excited $^{1}G_4$ multiplet of Pr$^{3+}$ in various, lightly doped, crystals have been studied. For all investigated systems, maximum of the $^{1}G_4-^{3}H_5$ emission is in the 1.35μm band. It was found that the $^{1}G_4$ decay is mostly nonradiative, except for LaF$_3$, for which the radiative contribution is not negligible and may be affected by cross-relaxation at higher activator concentrations.

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We thank Z.Frukacz from the ITME lab. (Warsaw), R.M. Macfarlane from IBM (San Jose), S.Payne from LLNL (Livermore) and J.C.Vial from the "Spectrometrie Physique" lab. (Grenoble) for providing us with the YAG, YAP, YLF and LaF$_3$ crystals, respectively.

References